



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 193 368
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 86301294.4

(51) Int. Cl.⁴: **C 07 C 51/285**
C 07 C 63/33, C 07 C 63/46
//B01J23/84

(22) Date of filing: 24.02.86

(30) Priority: 25.02.85 JP 34498/85
14.06.85 JP 128291/85
14.01.86 JP 4273/86

(43) Date of publication of application:
03.09.86 Bulletin 86/36

(84) Designated Contracting States:
DE FR GB IT NL

(71) Applicant: Nippon Shokubai Kagaku Kogyo Co., Ltd
1, 5-chome, Koraibashi Higashi-ku
Osaka(JP)

(71) Applicant: NIHON JYORYU KOGYO CO., LTD.
9-1, Koya-Shinmachi
Ichikawa-shi Chiba-ken(JP)

(72) Inventor: Salto, Yoshinori
15-6, Minamiyawata 1-chome
Ichikawa-shi Chiba-ken(JP)

(72) Inventor: Araki, Shinichi
12-11, Ichinoe 7-chome
Edogawa-ku Tokyo(JP)

(72) Inventor: Sugita, Yoshio
7-3, Chishirodai Higashi 3-chome
Chiba-shi Chiba-ken(JP)

(72) Inventor: Kurata, Naoji
9-23, Atagoyama
Nishinomiya-shi Hyogo-ken(JP)

(74) Representative: Myerscough, Philip Boyd et al,
J.A.Kemp & Co. 14, South Square Gray's Inn
London, WC1R 5EU(GB)

(54) Process for producing aromatic dicarboxylic acids.

(57) A process for producing an aromatic dicarboxylic acid which comprises subjecting a "K-region" arene to liquid phase oxidation with hydrogen peroxide in a water-insoluble organic solvent in the presence of a tungsten compound and a phase transfer catalyst and optionally a mineral acid.

EP 0 193 368 A1

Process for producing aromatic dicarboxylic acids

This invention relates to a process for producing an aromatic dicarboxylic acid, and more particularly to a process for producing an aromatic dicarboxylic acid in high yield which comprises subjecting a "K-region" arene to liquid phase oxidation with hydrogen peroxide in a water-insoluble organic solvent in the presence of a tungsten compound and a phase transfer catalyst.

As a method for producing aromatic dicarboxylic acids, e.g. biphenyl-2,2'-dicarboxylic acid, a method is known which comprises subjecting phenanthrene or 9,10-phenanthrenequinone, an oxidized product of phenanthrene to liquid phase oxidation with chromic acid or a bichromate. There are proposed other methods, i.e. a gaseous phase catalytic oxidation method of phenanthrene using a vanadium-type solid catalyst, and a liquid phase oxidation method such as an oxidation method using a permanganate, an oxidation method in aliphatic organic carboxylic acids using hydrogen peroxide or an organic peroxide and an ozone oxidation method.

Regarding a method for producing phenanthrene-4,5-dicarboxylic acid, there is very little literature, and a method wherein pyrene is oxidized with hydrogen peroxide via ozonolysis is only known [see Bulletin des Societes Chimiques Belges, vol. 72, pp. 289-290, 1963].

The above method for producing biphenyl-2,2'-dicarboxylic acid however suffers the problems to follow. That is, in the method using a chromium compound as an oxidizing agent, discharging of the chromium compound outside the system is severely restricted in the aspects of the prevention of environmental pollution and the environmental health. The use of the chromium compound in a closed system and a higher standard of working environment are therefore required, involving an enormous cost. Not only that, but incorporation of the chromium compound into products is unavoidable. Other methods

have also defects that the yield is low, oxidizing agents are expensive and corrosion of apparatuses is unescapable. Consequently, these methods have not come to be effective industrial methods.

5 In accordance with the foregoing method for producing phenanthrene-4,5-dicarboxylic acid, phenanthrene-4,5-dicarboxylic acid is obtained only in low yield of 28% by ozonizing pyrene and then oxidizing the resulting substance with hydrogen peroxide in a
10 sodium hydroxide-alcohol solvent at a low temperature of -20°C. This method therefore cannot be actually industrialized because of complicated operation and low yield.

The present inventors have made extensive
15 studies on a process for producing aromatic dicarboxylic acids economically advantageously, and as a result found a process wherein aromatic dicarboxylic acids can be produced from "K-region" arenes in high yields.

Thus, the present invention provides a process
20 for producing an aromatic dicarboxylic acid in high yield in a simple manner by subjecting a "K-region" arene to liquid phase oxidation with hydrogen peroxide in a water-insoluble organic solvent in the presence of a tungsten compound and a phase transfer catalyst
25 and optionally a mineral acid.

Most of the "K-region" arenes used in this invention are compounds obtained from coal tar or derivatives thereof. The starting material in the process of this invention is preferably at least one
30 compound selected from the group consisting of phenanthrene, pyrene, benzo[a]pyrene, benz[a]anthracene, benz[a,h]anthracene, chrysene and o-phenanthroline. Preferably, the "K-region" arenes have high purity, but considering economics the purity may be more than 80%,
35 specifically more than 90%. This is because even if products obtained by oxidizing impurities of the "K-region" arenes with hydrogen peroxide are partially

incorporated into the resulting aromatic dicarboxylic acids, they can easily be removed, if necessary, by a simple purification step.

5 The tungsten compound used in this invention is preferably an oxygen-containing hexavalent tungsten compound. Examples of said compound are tungstic acid and alkali salts (e.g. sodium salts and potassium salts) and ammonium salts thereof.

10 When phenanthrene is used as a starting material in the process of this invention, heteropoly-acid tungsten compounds such as phosphotungstic acid, silicotungstic acid, arsenotungstic acid, stannotungstic acid, germanotungstic acid, and alkali metal salts and ammonium salts of these compounds are also available as
15 the tungsten compound.

These tungsten compounds can be used such that they are dissolved or partially suspended in a reaction solution. The amount of the tungsten compound used is 0.005 to 0.2 gram atom, preferably 0.01 to 0.1 gram
20 atom, as a tungsten atom, per mol of the "K-region" arene. Where the amount is less than 0.01 gram atom, the oxidation reaction does not proceed enough. Where the amount is more than 0.1 gram atom, decomposition of hydrogen peroxide goes drastic, inviting a disadvantage
25 of losing the efficiency of hydrogen peroxide.

The phase transfer catalyst used in this invention is at least one substance selected from the group consisting of quaternary ammonium salts, quaternary phosphonium salts, quaternary arsonium salts, tertiary
30 amines, tertiary phosphines and tertiary arsines. Examples of the quaternary ammonium salts are trimethyl-alkylammonium halides, trialkylmethylammonium halides and pyridinium compounds. Most preferable are alkyl-trimethylammonium chlorides, trialkylmethylammonium
35 chlorides and alkylpyridinium chlorides wherein the number of carbon atoms of alkyl groups is 8 to 18. Examples of the quaternary phosphonium salts are alkyl-

triphenylphosphonium halides. Examples of the quaternary arsonium salts are alkyltriphenylarsonium halides. Examples of the tertiary amines are trialkylamines and methyldialkylamines. Most preferable are trialkylamines and methyldialkylamines wherein the number of carbon atoms of alkyl groups is 4 to 18. Examples of the tertiary phosphines are trialkylphosphines. Examples of the tertiary arsines are trialkylarsines. The amount of the phase transfer catalyst is 0.2 to 5 mol, preferably 0.5 to 2 mol per gram atom of tungsten.

It has been found for the first time that in producing the aromatic dicarboxylic acids by the oxidation of the "K-region" arenes with hydrogen peroxide, the use of tungsten compounds alone as the catalyst does not allow the oxidation reaction, but when the phase transfer catalyst is co-existent, the oxidation reaction smoothly advances, and the "K-region" arenes are converted into aromatic dicarboxylic acids in high selectivity.

In this invention, when the "K-region" arene is oxidized with hydrogen peroxide in the water-insoluble organic solvent in the presence of the tungsten compound as the catalyst and the phase transfer catalyst, controlling an acidity in the reaction system has a serious influence on the progress of the oxidation reaction. That is, where the reaction is further performed in an acid zone by causing a mineral acid to exist, conversion of the "K-region" arene into the aromatic dicarboxylic acid is expedited, thereby lessening the amount of hydrogen peroxide used. The mineral acid used is at least one compound selected from the group consisting of sulfuric acid, phosphoric acid and arsenic acid. The amount of the mineral acid is 0.1 to 20 mols per gram atom of tungsten.

The water-insoluble organic solvent may be any solvent substantially immiscible with an aqueous phase containing hydrogen peroxide and inactive in the reaction

system. Examples of said solvent are aliphatic hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons, and halogenated substances and esters of these hydrocarbons. Especially, the aliphatic hydrocarbons, aromatic hydrocarbons and halogenated substances of these hydrocarbons are preferable. The amount of the water-insoluble organic solvent is 0.5 to 10 parts by weight, preferably 1 to 5 part by weight per part by weight of the "K-region" arene considering the stirring conditions during the oxidation reaction, solubility of the resulting aromatic dicarboxylic acid in the water-insoluble organic solvent and withdrawing of the aromatic dicarboxylic acid precipitated.

A hydrogen peroxide aqueous solution in any concentration is available as hydrogen peroxide. Taking account of the fact that as the concentration is higher the oxidation reaction proceeds more smoothly, as well as of the handling and the availability of commercial products, the hydrogen peroxide aqueous solution is used in a concentration of 20 to 90%, preferably 40 to 70%. The amount of hydrogen peroxide may be more than a stoichiometric amount because the "K-region" arene consumed is converted into the aromatic dicarboxylic acid in high selectivity. It is usually 4 to 30 mols, preferably 6 to 10 mols per mol of the "K-region" arene.

The reaction can be performed at temperatures in the range of room temperature to 120°C. In consideration of the control of the oxidation reaction and the reaction time, the reaction temperature is commonly selected from the range of 50 to 100°C. The reaction time is usually 1 to 20 hours. The pressure in the reaction system may be an increased pressure, a normal pressure or a pressure lower than atmospheric pressure. The reaction can be carried out either batchwise or continuously.

The tungsten compounds and other transition metal compounds are known as effective catalysts for

hydroxylation, epoxidation and carboxylation with oxidative cleavage of varied organic compounds using hydrogen peroxide, organic peracids or peroxides as an oxidizing agent. However, a process that can produce aromatic dicarboxylic acids in high yields and high selectivity from "K-region" arenes such as phenanthrene, pyrene, etc. using these catalysts has not yet been known. The present invention has enabled this process for the first time by oxidizing the "K-region" arene with hydrogen peroxide in the water-insoluble organic solvent using the tungsten compound as the catalyst in combination with the phase transfer catalyst. It has moreover brought forth such dramatic effects that the conversion of the "K-region" arene into the aromatic dicarboxylic acid is rapidly improved by causing the mineral acid to exist in the reaction system for controlling the reaction in the acid zone, and the aromatic dicarboxylic acid is afforded in quite high yield.

20 The process of this invention is, though not restrained by a principle, presumed to be such that the tungsten compound as one component of the catalyst is converted into a water-soluble tungsten peroxide by decomposition with hydrogen peroxide and in a non-uniform phase composed of an aqueous phase containing those substances and an oily phase containing a substantially immiscible inactive organic solvent and the "K-region" arene, the active oxygen of tungsten peroxide serves to oxidize the "K-region" arene by the action of the phase transition catalyst, thereby facilitating the conversion of the "K-region" arene into the aromatic dicarboxylic acid. In case the reaction system is controlled in the acid zone by causing a mineral acid such as sulfuric acid, phosphoric acid or arsenic acid to exist in the reaction system, the decomposition of hydrogen peroxide is slowed down and the ability of the phase transfer catalyst in the non-uniform phase increases.

According to this invention, the "K-region" arene is converted into the aromatic dicarboxylic acid in high selectivity by the oxidation with hydrogen peroxide, and as a result crystals of the aromatic dicarboxylic acid can be afforded in high yield and high purity only by simple steps of cooling and separation by filtration after termination of the reaction. Moreover, in order to remove oxides derived from impurities of the starting "K-region" arene and contained in the resulting crystals, said crystals are, if necessary, extracted with an alkali aqueous solution by suspending or dissolving in an organic solvent, precipitated with an acid, separated by filtration and dried. The aromatic dicarboxylic acid in high purity of more than 99% can be obtained with little loss by the foregoing simple operation.

The following Examples illustrate this invention more specifically. However, this invention is, of course, not limited to said Examples.

In said Examples, the conversion of phenanthrene, the selectivity to biphenyl-2,2'-dicarboxylic acid, the conversion of pyrene and the selectivity to phenanthrene-4,5-dicarboxylic acid are found by the following equations.

$$\begin{aligned}
 \text{Conversion of phenanthrene (\%)} &= \frac{\text{Amount of phenanthrene consumed (mol)}}{\text{Amount of phenanthrene charged (mol)}} \times 100 \\
 \text{Selectivity to biphenyl-2,2'-dicarboxylic acid (\%)} &= \frac{\text{Amount of biphenyl-2,2'-dicarboxylic acid formed (mol)}}{\text{Amount of phenanthrene consumed (mol)}} \times 100 \\
 \text{Conversion of pyrene (\%)} &= \frac{\text{Amount of pyrene consumed (mol)}}{\text{Amount of pyrene charged (mol)}} \times 100 \\
 \text{Selectivity to phenanthrene-4,5-dicarboxylic acid (\%)} &= \frac{\text{Amount of phenanthrene-4,5-dicarboxylic acid formed (mol)}}{\text{Amount of pyrene consumed (mol)}} \times 100
 \end{aligned}$$

Example 1:

25.0g of 90.6% phenanthrene, 1.27g of tungstic acid, 2.05g of tri-n-octylmethylammonium chloride and 38g of monochlorobenzene were charged into a 300 cc four-necked round bottom glass flask fitted with a thermometer, a cooler and a stirrer, and heated to 80°C in a hot bath with vigorous stirring. Subsequently, 143.4g of a 60.2% hydrogen peroxide aqueous solution was added dropwise with a glass dropping funnel over the course of 30 minutes, and the mixture was maintained for 6 hours. During that period, the pH of the reaction solution was 0.5 or less.

After the reaction terminated, the content was analyzed by high performance liquid chromatography and gas chromatography. The results are as follows.

Conversion of phenanthrene	39.0%
Selectivity to biphenyl-2,2'-dicarboxylic acid	97.2%

Example 2:

The procedure in Example 1 was followed except using 1.34g of lauryltrimethylammonium chloride instead of tri-n-octylmethylammonium chloride. During the reaction, the pH of the reaction solution was 1.1 or less.

Conversion of phenanthrene	31.8%
Selectivity to biphenyl-2,2'-dicarboxylic acid	97.5%

Example 3:

The procedure in Example 1 was followed except using 1.44g of laurylpyridinium chloride instead of tri-n-octylmethylammonium chloride. During the reaction, the pH of the reaction solution was 3.5 or less.

Conversion of phenanthrene	21.3%
Selectivity to biphenyl-2,2'-dicarboxylic acid	98.2%

Example 4:

The procedure in Example 1 was followed except using 2.28g of triphenylmethylarsonium iodide instead of

tri-n-octylmethylammonium chloride. During the reaction, the pH of the reaction solution was 6.6 or less.

Conversion of phenanthrene	17.8%
Selectivity to biphenyl-2,2'-dicarboxylic acid	97.7%

5 Example 5:

The procedure in Example 1 was followed except that the amount of tungstic acid was changed into 1.59g and 2.25g of tri-n-octylamine was used instead of tri-n-octylmethylammonium chloride. During the reaction, the pH of the reaction solution was 1.1 or less.

Conversion of phenanthrene	73.7%
Selectivity of biphenyl-2,2'-dicarboxylic acid	95.7%

Example 6:

The procedure in Example 5 was repeated except that 1.62g of N-methyl-di-n-octylamine was used instead of tri-n-octylamine. During the reaction, the pH of the reaction solution was 1.1 or less.

Conversion of phenanthrene	76.2%
Selectivity to biphenyl-2,2'-dicarboxylic acid	96.0%

20 Example 7:

The procedure in Example 5 was repeated except that 2.35g of tri-n-octylphosphine was used instead of tri-n-octylamine. During the reaction, the pH of the reaction solution was 1.4 or less.

Conversion of phenanthrene	65.0%
Selectivity to biphenyl-2,2'-dicarboxylic acid	92.2%

Example 8:

The procedure in Example 1 was repeated except that 25.0g of 92.3% pyrene was used instead of phenanthrene, and the amount of tungstic acid was changed into 1.14g, the amount of tri-n-octylmethylammonium chloride into 1.84g, the amount of monochlorobenzene into 67g and the amount of the 60.2% hydrogen peroxide aqueous solution into 128.7g respectively. During the reaction,

the pH of the reaction solution was 2.2 or less.

Conversion of pyrene	43.2%
Selectivity to phenanthrene-4,5-dicarboxylic acid	78.6%

Example 9:

5 The procedure in Example 8 was repeated except that 1.20g of lauryltrimethylammonium chloride was used instead of tri-n-octylmethylammonium chloride. During the reaction, the pH of the reaction solution was 2.5 or less.

10 Conversion of pyrene	35.7%
Selectivity to phenanthrene-4,5-dicarboxylic acid	74.2%

Example 10:

15 The procedure in Example 8 was repeated except that 1.29g of laurylpyridinium chloride was used instead of tri-n-octylmethylammonium chloride. During the reaction, the pH of the reaction solution was 3.8 or less.

Conversion of pyrene	26.4%
Selectivity to phenanthrene-4,5-dicarboxylic acid	73.0%

Example 11:

20 The procedure in Example 8 was repeated except that 2.05g of triphenylmethylarsonium iodide was used instead of tri-n-octylmethylammonium chloride. During the reaction, the pH of the reaction solution was 6.2 or less.

25 Conversion of pyrene	20.7%
Selectivity to phenanthrene-4,5-dicarboxylic acid	71.3%

Example 12:

30 The procedure in Example 8 was repeated except that the amount of rungstic acid was changed into 1.42g and 2.02g of tri-n-octylamine was used instead of tri-n-octylmethylammonium chloride. During the reaction, the pH of the reaction solution was 1.9 or less.

Conversion of pyrene	85.0%
Selectivity to phenanthrene-4,5-dicarboxylic acid	74.8%

Example 13:

The procedure in Example 12 was repeated except that 1.46g of N-methyl-di-n-octylamine was used instead of tri-n-octylamine. During the reaction, the pH of the reaction solution was 1.8 or less.

Conversion of pyrene	83.6%
Selectivity to phenanthrene-4,5-dicarboxylic acid	75.4%

Example 14:

25.0g of 90.6% phenanthrene, 1.27g of tungstic acid, 2.05g of tri-n-octylmethylammonium chloride, 1.2 cc of 10% phosphoric acid and 38g of monochlorobenzene were charged into a 300 cc four-necked round bottom glass flask fitted with a thermometer, a cooler and a stirrer, and heated to 80°C in a hot bath with vigorous stirring. 50.2g of a 60.2% hydrogen peroxide aqueous solution was then added dropwise from a glass dropping funnel over the course of 30 minutes, and the mixture was maintained for 6 hours. During that period, the pH of the reaction solution was 0.5 or less. The subsequent operation was performed in the same way as in Example 1.

Conversion of phenanthrene	99.6%
Selectivity to biphenyl-2,2'-dicarboxylic acid	99.1%

Example 15:

The procedure in Example 14 was followed except that 0.3 cc of 60% arsenic acid was used instead of 10% phosphoric acid. During the reaction, the pH of the reaction solution was 0.5 or less.

Conversion of phenanthrene	98.8%
Selectivity to biphenyl-2,2'-dicarboxylic acid	99.4%

Example 16:

The procedure in Example 14 was followed except that 8 cc of 30% sulfuric acid was used instead of 10% phosphoric acid. During the reaction, the pH of the reaction solution was 0.5 or less.

Conversion of phenanthrene	75.7%
----------------------------	-------

Selectivity to	
biphenyl-2,2'-dicarboxylic acid	98.3%

Example 17:

The procedure in Example 14 was followed except that 1.34g of lauryltrimethylammonium chloride was used instead of tri-n-octylmethylammonium chloride. During the reaction, the pH of the reaction solution was 0.5 or less.

Conversion of phenanthrene	97.9%
Selectivity to	
biphenyl-2,2'-dicarboxylic acid	98.8%

10 Example 18:

The procedure in Example 14 was followed except that 1.68g of sodium tungstate dihydrate was used instead of tungstic acid and the amount of 10% phosphoric acid was changed into 4 cc. During the reaction, the pH of the reaction solution was 0.9 or less.

Conversion of phenanthrene	93.2%
Selectivity to	
biphenyl-2,2'-dicarboxylic acid	97.6%

Example 19:

20 The procedure in Example 18 was followed except that 8 cc of 30% sulfuric acid was used instead of 10% phosphoric acid. During the reaction, the pH of the reaction solution was 1.2 or less.

Conversion of phenanthrene	63.2%
Selectivity to	
biphenyl-2,2'-dicarboxylic acid	97.8%

25 Example 20:

The procedure in Example 18 was followed except that 1.33g of ammonium paratungstate was used instead of sodium tungstate dihydrate. During the reaction, the pH of the reaction solution was 0.9 or less.

Conversion of phenanthrene	97.5%
Selectivity to	
biphenyl-2,2'-dicarboxylic acid	98.3%

Example 21:

The procedure in Example 14 was followed

except that the amount of tungstic acid was changed into 1.59g, 2.25g of tri-n-octylamine was used instead of tri-n-octylmethyammonium chloride and the amount of 10% phosphoric acid was changed into 1.5 cc. During the reaction, the pH of the reaction solution was 0.8 or less.

Conversion of phenanthrene	96.1%
Selectivity to biphenyl-2,2'-dicarboxylic acid	98.9%

Example 22:

The procedure in Example 21 was followed except that 1.62g of N-methyl-di-n-octylamine was used instead of tri-n-octylamine. During the reaction, the pH of the reaction solution was 0.9 or less.

Conversion of phenanthrene	98.4%
Selectivity to biphenyl-2,2'-dicarboxylic acid	98.2%

Example 23:

The procedure in Example 21 was followed except that 0.4 cc of 60% arsenic acid was used instead of 10% phosphoric acid. During the reaction, the pH of the reaction solution was 1.0 or less.

Conversion of phenanthrene	88.8%
Selectivity to biphenyl-2,2'-dicarboxylic acid	94.7%

Example 24:

The procedure in Example 21 was followed except that 8 cc of 30% sulfuric acid was used instead of 10% phosphoric acid. During the reaction, the pH of the reaction solution was 0.7 or less.

Conversion of phenanthrene	91.2%
Selectivity to biphenyl-2,2'-dicarboxylic acid	96.2%

Example 25:

The procedure in Example 24 was followed except that 2.09g of sodium tungstate dihydrate was used instead of tungstic acid. During the reaction, the pH of the reaction solution was 0.8 or less.

Conversion of phenanthrene	87.9%
Selectivity to biphenyl-2,2'-dicarboxylic acid	94.6%

Example 26:

The procedure in Example 21 was followed except that 1.60g of ammonium paratungstate was used instead of tungstic acid and the amount of 10% phosphoric acid was changed into 6 cc. During the reaction, the pH of the reaction solution was 1.5 or less.

Conversion of phenanthrene	85.0%
Selectivity to biphenyl-2,2'-dicarboxylic acid	95.1%

Example 27:

The procedure in Example 16 was followed except that 25.0g of 92.3% pyrene was used instead of phenanthrene, and the amount of tungstic acid was changed into 1.14g, the amount of tri-n-octylmethylammonium chloride into 1.84g, the amount of monochlorobenzene into 67g and the amount of the 60.2% hydrogen peroxide aqueous solution into 45.1g respectively. During the reaction, the pH of the reaction solution was 1.4 or less.

Conversion of pyrene	93.0%
Selectivity to phenanthrene-4,5-dicarboxylic acid	70.5%

Example 28:

The procedure in Example 27 was followed except that 0.3 cc of 60% arsenic acid was used instead of 30% sulfuric acid. During the reaction, the pH of the reaction solution was 1.4 or less.

Conversion of pyrene	98.4%
Selectivity to phenanthrene-4,5-dicarboxylic acid	78.8%

Example 29:

The procedure in Example 27 was followed except that 1.1 cc of 10% phosphoric acid was used instead of 30% sulfuric acid. During the reaction, the pH of the reaction solution was 0.7 or less.

Conversion of pyrene	99.2%
Selectivity to phenanthrene-4,5-dicarboxylic acid	81.3%

Example 30:

5 The procedure in Example 29 was followed except that 1.20g of laurylmethylammonium chloride was used instead of tri-n-octylmethylammonium chloride. During the reaction, the pH of the reaction solution was 2.0 or less.

10	Conversion of pyrene	92.5%
	Selectivity to phenanthrene-4,5-dicarboxylic acid	78.9%

Example 31:

15 The procedure in Example 29 was followed except that 1.51g of sodium tungstate dihydrate was used instead of tungstic acid and the amount of 10% phosphoric acid was changed into 4 cc. During the reaction, the pH of the reaction solution was 1.9 or less.

Conversion of pyrene	92.2%
Selectivity to phenanthrene-4,5-dicarboxylic acid	80.7%

Example 32:

20 The procedure in Example 27 was followed except that 1.51g of sodium tungstate dihydrate was used instead of tungstic acid. During the reaction, the pH of the reaction solution was 2.3 or less.

25	Conversion of pyrene	64.1%
	Selectivity to phenanthrene-4,5-dicarboxylic acid	73.8%

Example 33:

30 The procedure in Example 31 was followed except that 1.17g of ammonium paratungstate was used instead of sodium tungstate dihydrate. During the reaction, the pH of the reaction solution was 1.5 or less.

Conversion of pyrene	95.4%
Selectivity to phenanthrene-4,5-dicarboxylic acid	79.5%

Example 34:

The procedure in Example 29 was followed except that the amount of tungstic acid was changed into 1.42g, 2.02g of tri-n-octylamine was used instead of tri-n-octylmethyammonium chloride, and the amount of 10% phosphoric acid was changed into 1.4 cc. During the reaction, the pH of the reaction solution was 1.5 or less.

	Conversion of pyrene	97.1%
10	Selectivity to phenanthrene-4,5-dicarboxylic acid	80.6%

Example 35:

The procedure in Example 34 was followed except that 1.46g of N-methyl-di-n-octylamine was used instead of tri-n-octylamine and 8 cc of 30% sulfuric acid instead of 10% phosphoric acid, respectively. During the reaction, the pH of the reaction solution was 1.6 or less.

	Conversion of pyrene	88.0%
	Selectivity to phenanthrene-4,5-dicarboxylic acid	72.7%

- 17 -

CLAIMS

1. A process for producing an aromatic dicarboxylic acid which comprises subjecting a "K-region" arene to liquid phase oxidation with hydrogen peroxide in a water-insoluble organic solvent in the presence of a tungsten compound and a phase transfer catalyst.
5
2. A process of claim 1 wherein the tungsten compound is an oxygen-containing hexavalent tungsten compound and is used in an amount of 0.005 to 0.2 gram atom, as tungsten atom, per mol of the "K-region" arene.
- 10 3. A process according to claim 1 wherein the liquid phase oxidation is carried out in an acid zone in the presence of a mineral acid.
4. A process according to claim 3 wherein the tungsten compound is at least one of tungstic acid, and sodium salts, potassium salts and ammonium salts thereof,
15 and is used in an amount of 0.005 to 0.2 gram atom, as tungsten atom, per mol of the "K-region" arene.
5. A process according to claim 3 or 4 wherein the mineral acid is at least one of sulfuric acid, phosphoric acid and arsenic acid, and is used in an amount of 0.1 to 20
20 mols per gram atom of tungsten.
6. A process according to any one of the preceding claims wherein the "K-region" arene is at least one of phenanthrene, pyrene, benzo[a]pyrene, benz[a]anthracene, dibenz[a,h]anthracene, chrysene and o-phenanthroline.
25
7. A process according to any one of the preceding claims wherein the phase transfer catalyst is at least one of quaternary ammonium salts, quaternary phosphonium salts, quaternary arsonium salts, tertiary amines, tertiary phosphines and tertiary arsines, and is used in an amount of
30 0.2 to 5 mol per gram atom of tungsten.
8. A process according to any one of the preceding claims wherein the water-insoluble organic solvent is selected from aliphatic hydrocarbons, aromatic hydrocarbons

- 18 -

and halogenated substances of these hydrocarbons, and is used in an amount of 0.5 to 10 parts by weight per part by weight of the "K-region" arene.

9. A process according to any one of the preceding
- 5 claims wherein the aromatic dicarboxylic acid is biphenyl-2,2'-dicarboxylic acid or phenanthrene-4,5-dicarboxylic acid.



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 86301294.4
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	CHEMICAL ABSTRACTS, vol. 59, no. 4, August 19, 1963, Columbus, Ohio, USA C.DANHEUX et al. "Ozonolysis of pyrene to phenanthrene-4,5-dicarboxylic acid" column 3848e X	1,6,9	C 07 C 51/285 C 07 C 63/33 C 07 C 63/46 //B 01 J 23/84
D	Bull. Soc. Chim. Belges <u>72</u> , 289-90(1963)		
A	GB - A - 853 369 (RUTGERSWERKE-AG) * Examples *	1,6,8,9	
A	EP - A1 - O 123 495 (MONTEDISON S.P.A.) * Claims *	1-5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 C 51/00 C 07 C 63/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 30-04-1986	Examiner HOFBAUER
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPD Form 1503 (3/82)